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(54) **Ceramic binder and use thereof.**

(57) Ceramic binder for forming and processing ceramic ware, comprising a sol-gel of a mixture of highly charged metal hydroxy cations and one or more low charged metal hydroxy cations, which are able to form an aqueous sol.

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The present invention is related to a ceramic binder, and more particularly, to a ceramic binder, which enables forming and processing of large defect-free ceramic ware with complex shape.

Forming processes most commonly used in the manufacture of ceramic ware are cold forming processes, including extrusion or dry pressing and slip casting at ambient temperature.

Extrusion and dry pressing methods are commonly used, when ceramic articles with simple shapes are to be formed.

Ceramic articles with more complex shapes are formed by slip casting.

In slip casting, usually a suspension of solid particles of ceramic materials in water is poured into a porous mold of Paris plaster, wherein formation is accomplished by consolidation of the particles into a semirigid state through removal of a part of the water by rehydration of the plaster.

Drying of the cast articles represents a critical operation in the finishing of the articles. The water has to be removed carefully without introducing defects into the green ceramic caused by shrinkage during dewatering. In order to reduce cracking or distortion of the green ceramic usual drying times are in the order of 5-7 days for one centimeter thickness of the green ceramic component.

We have now found that the drying time during the preparation of advanced ceramic components can be much decreased, when using a ceramic binder comprising a sol-gel of highly charged particles and particles with a lower specific charge.

Accordingly, a broad embodiment of this invention is directed towards a ceramic binder comprising a sol-gel of a mixture of highly charged metal hydroxy cations and one or more low charged metal hydroxy cations, which are able to form an aqueous sol.

Low charged metal hydroxy cations for use in the ceramic binder are preferably chosen from the group consisting of the hydroxides of aluminum, silicon, zirconium, titanium, iron and nickel.

A particular preferred ceramic binder according to the invention comprises a sol-gel of aluminium hydroxide with the boehmite structure, mixed with highly charged aluminum tridecamer, having the general formula:

$$[AlO_4Al_{12}(OH)_{24} \cdot 20H_2O]^{7+}, 7X^-$$

where

$X = Cl^-$, or NO_3^-

The ceramic binder according to the invention is obtained by preparing a sol of salts of the low charged metal hydroxy cations in water, which has been acidified by addition of hydrochloric acid or nitric acid to a pH-value of between 1.5 and 4;

activating the sol by heating to a temperature of between 70 °C and 100 °C at a pH-value of between 1.5 and 4, preferably of between 2-3, for 2-6 hours until a sol-gel of 3-12% by weight is obtained;

optionally filtering the sol-gel; then

adding to the sol-gel an aqueous solution of salts of highly charged metal hydroxy cations containing 0.05-10 g, preferably 0.1-3 g, and most preferred 0.5-2 g of the salts per 10 g of the salts of the low charged cations in the sol-gel; and

continuing heating of the sol-gel for about one hour at a pH-value of between 1.5 and 4.

When used in the forming of ceramic components by slip casting, ceramic materials comprising powders and/or fibres of refractory oxides, such as alumina, silica, chromia, zirconia, nickel oxides and the like, are dispersed in the ceramic binder in an amount of up to 90% by weight calculated on the total amount of binder and ceramic materials. Thereby, a casting slip is obtained, which can be demolded after about 30 minutes in the mold and machined after about 3 hours, when dried at temperatures of between 20 °C and 60 °C. Some further drying of up to 1½ day for large samples may be preferred.

The dried green ceramic thus obtained is finally densified by conventional sintering.

As mentioned hereinbefore the drying time of green ceramics before sintering is reduced from 5-7 days as for green ceramic prepared without the ceramic binder according to the invention to about 3-36 hours by use of the ceramic binder. The actual drying time length depends upon the ceramic material used in the casting slip and the shape and size of the green ceramic.

As a further advantage of the ceramic binder according to the invention, defects in the green ceramic can be repaired by simply filling with the binder cracks or distortion in the casting slip or dried green ceramic.

The above aspects and features of this invention will become more apparent by the following Examples, illustrating specific embodiments of the invention.

Example 1

Preparation of a ceramic binder according to the invention comprising a low charged metal hydroxy cation with the boehmite structure and aluminum tridecamer.

A boehmite sol is prepared by adding 10 g of commercial boehmite powder (Catapal D, supplied by Vista Chemical Company, U.S.A.) to a stirred beaker with 1000 ml demineralized water acidified with nitric acid to a pH-value of 2.

The prepared boehmite sol is activated by heating to 80-90 °C for about 3-5 hours until a 6-10% by weight sol-gel is obtained. During activation the pH-value of the sol is continously adjusted to pH 2 by dropwise addition of concentrated nitric acid.

The sol-gel is then purified by filtration to remove extraneous particles.

The final binder is prepared by adding to the sol-gel 2 g of a 50% by weight solution of aluminum tridecamer (Locron S, supplied by Hoechst AG, Germany) and continuing heating for 1 hour at pH 2-3.

Example 2

Preparation of a ceramic body by use of the ceramic binder according to the invention.

An alumina casting slip is prepared by adding alumina powder (Alcoa A 16 SG, Alcoa Company, U.S.A.) to a stirred beaker containing the boehmite binder prepared in Example 1. The alumina powder is added to the binder until a casting slip with 85% by weight of the alumina powder is obtained.

The thus prepared casting slip is poured into a mold of Paris plaster with a rectangular interior surface of 2 cm in height. The slip is demolded after about 30 minutes at room temperature, machined for holes after 3 hours, then dried for additionally 20 hours at a temperature of 50 °C. The green body is subsequently sintered at 1550 °C for two hours.

The strength and toughness of the sintered ceramic body is tested in a conventional 4 point bending test and a Vickers hardness test equipped with a diamond pyramid having a tip angle of 136 degrees.

The results of the tests are summarized below.

Properties of alumina ceramic prepared in the Example:

Strength MPa	Fracture toughness MPa $m^{\frac{1}{2}}$
287	5

The corresponding value for the strength of conventionally prepared ceramic ware is about 250 MPa, with a fracture toughness of about 3 MPa $m^{\frac{1}{2}}$.
(W.D. Kingery, Introduction to Ceramics, page 791, 2nd Edition 1976, John Wiley and Sons).

Claims

1. Ceramic binder for forming and processing ceramic ware, comprising a sol-gel of a mixture of highly charged metal hydroxy cations and one or more low charged metal hydroxy cations, which are able to form an aqueous sol.

2. The ceramic binder of claim 1, wherein the low charged metal hydroxy cations are selected from the group consisting of the hydroxides of aluminum, silicon, zirconium, titanium, iron and nickel.

3. The ceramic binder of claim 2, wherein the low charged metal hydroxy cation is aluminum hydroxide with the boehmite structure.

4. The ceramic binder of claim 1 and 2, wherein the highly charged metal hydroxy cation is an aluminum tridecamer with the general formula:

$$[AlO_4Al_{12}(OH)_{24} \cdot 20H_2O]^{7+}, 7X^-$$

where
X is Cl^-,
and/or

NO_3^-

5. The ceramic binder of claim 1, wherein the highly charged metal hydroxy cations constitute 0.05-7 g, preferably 0.1-3 g and most preferred 0.5-2 g per 10 g of the low charged metal hydroxy cations.

6. Process for the preparation of a ceramic binder according to anyone of the preceding claims, comprising the steps of preparing a sol of salts of low charged metal hydroxy cations in water, acidified with hydrochloric acid or nitric acid to a pH-value of between 1.5 and 4, preferably between 2 and 3;
activating the sol by heating to a temperature of between 70°C and 100°C at a pH-value of between 1.5 and 4, preferably 2 and 3, until a sol-gel with 3-12% by weight is obtained; and
optionally filtering the sol-gel; finally
adding to the sol-gel an aqueous solution of salts of highly charged metal hydroxy cations containing 0.05-7 g, preferably 0.1-3 g, and most preferred 0.5-2 g of the salt per 10 g of the salts of the low charged metal hydroxy cations in the sol-gel; and
continuing heating of the sol-gel for about one hour at a pH-value of between 1.5 and 4.

7. Use of the ceramic binder according to anyone of claims 1-5 in the forming and processing of ceramic ware by slip casting of ceramic material comprising powders and/or fibres of refractory oxides.

8. The use of claim 7, wherein the powder and/or fibres are dispersed in the ceramic binder in an amount of up to 90% by weight calculated on the total amount of binder powder and/or fibres.

9. The use of claim 7, wherein the processing of ceramic ware includes reparation and gluing of green ceramic ware.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 10 7222

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 116 436 (ALCAN INTERNATIONAL, LTD.) * page 2, line 13 - page 5, line 28; claims; examples *	1-2,7-9	C04B35/00 C01F7/02 C01F7/34 C04B35/10
A	US-A-4 720 302 (T.D.HUTCHINSON) * the whole document *	1-9	B01J20/08
A	DE-A-2 809 037 (SUMITOMO ALUMINIUM SMELTING CO., LTD.) * page 10, line 1 - line 6; claims *	3-6	
A	US-A-4 205 032 (I.R.WALTERS ET AL.)		
A	EP-A-0 113 796 (DEGUSSA AG)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C04B
C01F
B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06 AUGUST 1992	HARBRON J.L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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